## **EXHIBIT C**

## Synthesis and Odor Properties of Substituted Indane-2-carboxaldehydes. Discovery of a New Floral (Muguet) Fragrance Alcohol

by Béat Winter\* and Sandrine Gallo-Flückiger

Firmenich SA, Corporate R&D Division, P.O. Box 239, CH-1211 Geneva 8 (phone: +41227803612; fax: +41227803334; e-mail: beat.winter@firmenich.com)

Dedicated to Dr. Ferdinand Naef on the occasion of his 65th birthday

Eight substituted indane-2-carboxaldehydes (= 2,3-dihydro-1*H*-indene-2-carboxaldehydes), related to conformationally constrained analogues of floral-type odorants, were synthesized in order to examine the effect of modifying the lipophilic part of the odorants (*Schemes I* and 2). None of the modified compounds showed better olfactive properties than the original ones (*Tables I* and 2), but an intermediate alcohol, 29, revealed itself as a valuable new member in the family of floral muguet (lily-of-the-valley)-type odorants.

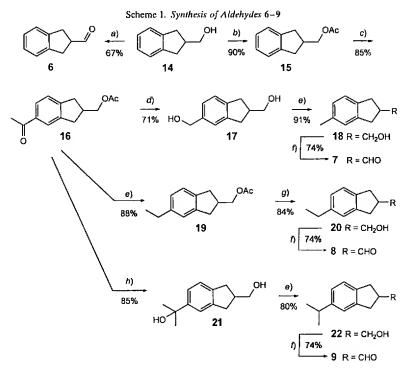
1. Introduction. – Previous studies [1] on conformationally constrained analogues of floral-type perfumery materials such as 1–3, have led to the discovery of new interesting odorants [2], among which compounds 4 and 5 were quite intriguing. Indeed, whereas compound 4 had an odor characterized as 'watery, metallic, aldehydic, green, somewhat fatty, vaguely phenolic', compound 5 was evaluated as typically 'floral, green, 'muguet', Bourgeonal®, powerful, tenacious' [1]. This result and related ones pointed to the importance of the steric constraints imposed by the receptor environment in the proximity of the ligand functional group.

On the other hand, we suspected that the lipophilic part of the ligands might also play a significant role in their distribution, their affinity, and their orientation in the relevant receptive sites [3]. Accordingly, we undertook to modify the lipophilic part in 4 and 5 and to prepare aldehydes 6 [4] – 13 via intermediates derived from 1H-indene. We describe in the present paper the synthesis and sensory characterization of this series of aldehydes and their precursor alcohols, which unveiled an olfactorily very interesting new compound.

**2. Results and Discussion.** -2.1. Syntheses. Aldehyde 6 was prepared by oxidation of alcohol 14 [4a,b,g][5]; as noted earlier [4c,f], 6 is very sensitive to oxidation by air. Aldehydes 7-9 were synthesized via the common key intermediate 16; this keto

ester was prepared from alcohol 14 by esterification to acetate 15 [4b] [5a] followed by Friedel-Crafts acylation, as shown in Scheme 1.

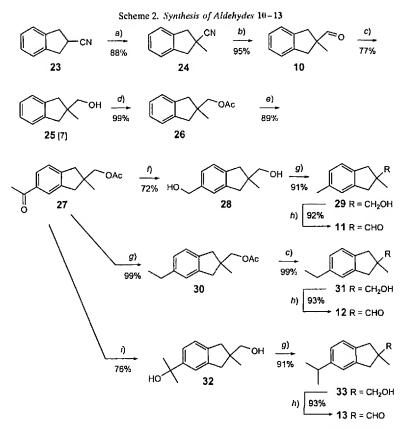
Compound 16 was subjected to the haloform reaction, followed by LiAlH<sub>4</sub> reduction to give diol 17, which was hydrogenolyzed ( $\rightarrow$  18), and then oxidized with pyridinium chlorochromate (PCC) to aldehyde 7. Next, 16 was hydrogenated to give ester 19, which was reduced to alcohol 20 and oxidized with PCC to aldehyde 8. Finally, *Grignard* reaction of 16 produced diol 21, which, as above, was hydrogenolyzed ( $\rightarrow$  22) and oxidized to afford aldehyde 9.



a) Pyridinium chlorochromate (PCC), CH<sub>2</sub>Cl<sub>2</sub>, r.t. b) Ac<sub>2</sub>O, pyridine, r.t., 3.5 h. c) AcCl, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0° → r.t., 1 h. d) 1. NaOCl, H<sub>2</sub>O, dioxane, 60°, 17 h; 2. LiAlH<sub>4</sub>, THF, reflux, 16 h. c) H<sub>2</sub> (1 atm), 10% Pd/C, AcOEt, r.t., 16 h. f) PCC, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 4 h. g) LiAlH<sub>4</sub>, Et<sub>2</sub>O, r.t., 1.5 h. h) MeMgCl, THF, r.t. → 60°, 2 h.

Turning then to the series of 2-methylindane-2-carboxaldehydes 10-13, the attempted alkylation of 6 gave 10 in only low yield and purity; aldehyde 10 was preferentially prepared in good yield by alkylation of nitrile 23 [6] ( $\rightarrow$  24), followed by reduction (*Scheme* 2). For the synthesis of aldehydes 11-13, we applied the same principle as above, which allowed to use the keto ester 27 as a common intermediate. Thus, 10 was reduced to alcohol 25 [7], which was esterified ( $\rightarrow$  26) and acylated to afford 27; from 27, aldehydes 11-13 were synthesized via 28-33 in the same manner as above.

2.2. Olfactory Evaluation. The results of the olfactory evaluation of aldehydes 6-13 are given in Table 1, and those of the alcohol precursors are shown in Table 2. The unexpected result of this work was the powerful floral muguet(lily-of-the-valley)-type odor



a) Lithium diisopropylamide (LDA), MeI, THF, -78° → r.t. → 50°, 1.5 h. b) Diisobutylaluminium hydride (DIBAL-H), toluene, r.t., 1.5 h. c) LiAlH4, Et<sub>2</sub>O, r.t., 15 h; d) Ac<sub>2</sub>O, pyridine, r.t., 36 h. e) AcCl, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0°, 1.5 h. f) 1. NaOCl, H<sub>2</sub>O, dioxane, 60°, 16 h; 2. LiAlH4, THF, reflux, 16 h. g) H<sub>2</sub> (1 atm), 10% Pd/C, AcOEt, r.t., 18 h. h) PCC, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 3 h. i) MeMgCl, THF, r.t. → 60°, 1.5 h.

of the intermediate alcohol 29 [8] (see *Table 2*), noticed as soon as we isolated it<sup>1</sup>). Quickly, however, the structural parenthood of alcohol 29 with the floral odorant *Majantol*<sup>®</sup> (34) [9] was recognized. In fact, alcohol 29 can be considered as a conformationally restricted analogue of 34, and the same relationship holds for alcohol 25 and the floral odorant 35, known as 'muguet alcohol' [9b][10].

Table 1. Odor Description of Aldehydes 6-13. Excepting 6 and 10, all compounds are racemates.

	Odor description	
6	'Aldehydic, green, grassy, ozonic, slightly metallic, cuminic, very powerful, aggressive'	
7	'Aldehydic, floral-muguet, soapy, fatty, slightly lemon'	
8	'Aldehydic, metallic, muguet, citrus'	
9	'Aldehydic, green, citrus, ozone, cyclamen aldehyde, metallic, Bourgeonal', but weaker'	
10	'Phenolic, aldehydic, green'	
11	'Aldehydic, green, Bourgeonal®, slightly fatty, fertilizer'	
12	'Aldehydic, metallic, fatty, perillic'	
13	'Aldehydic, metallic, ozone, green, citrus'	

Table 2. Odor Description of Precursor Alcohols 14, 18, 20, 22, 25, 29, 31, and 33. Excepting 14 and 25, all compounds are racemates.

	Odor description	
14	'Leather, old shoes, ammunition, fatty'	
18	'Floral, phenolic, fatty'	
20	'Odorless'	
22	'Odorless'	
25	'Floral, Lilial', muguet, hydroxycitronellal'	
29	'Liliat®, hydroxycitronellal, Mayol®, muguet'	
31	'Vaguely floral, weak'	
33	'Floral, linalool, very weak'	

In conclusion, none of the initially targeted aldehydes had better olfactive properties than the already established odorants of this class, but the intermediate alcohol 29 revealed itself as a valuable new member in the family of floral muguet(lily-of-the-valley)-type odorants [11].

We gratefully acknowledge the collaboration of Mr. W. Thommen and Mr. R. Brauchli for the NMR analysis. We wish to thank Dr. P.-A. Blunc for the evaluation of olfactory properties, and Dr. R. L. Snowden and Dr. C. Fehr for stimulating discussions.

See accompanying publication for an alternative synthesis of 29 and the characterization of the enantiomers of 29.

## **Experimental Part**

General. All reactions were performed under N<sub>2</sub> GLC: Hewlett-Packard 5890 or 6890 instrument equipped with a flame-ionization detector coupled to a Hewlett-Packard 3395 or 3396A integrator; capillary columns Chrompack CP-Wax-52 CB (10 m, 0.25 mm i.d.) and CP-Sil-5 CB (10 m, 0.25 mm i.d.). TLC: silica gel 60 F 254 (layer thickness 0.25 mm; Merck). Column chromatography (CC): silica gel 60 (0.063-0.2 mm, 70-270 mesh, ASTM; Merck). Bulb-to-bulb distillation: Būchi GKR-50 or GRK-51 oven; b.p. correspond to the air temp. IR Spectra (liquid film or solid): Perkin-Elmer 297 or 1600-FT1R spectrometers; v in cm<sup>-1</sup>. H- and <sup>13</sup>C-NMR Spectra (CDCl<sub>3</sub>): Bruker AMX-360, DPX-400, or AV-500 spectrometers; d in ppm downfield from SiMe<sub>3</sub>, J in Hz. MS: IIP 5972 or 5973 MSD (70 eV); in m/z (intensity in % rel. to the base peak (100%)).

- 1. General Procedure A (G.P.A) for the Hydrogenolysis of Benzylic Alcohols. To a soln, of the benzylic alcohol in AcOEt was added 10% Pd/C (ca. 0.02 equiv.), and the mixture was shaken under  $H_2$  (1 atm) at r.t. until no more starting material was detected by GC (16-46 h). The catalyst was filtered off and the filtrate evaporated.
- 2. General Procedure B (G.P.B) for the Oxidation of Alcohols to Aldehydes with Pyridinium Chlorochromate (PCC). To a stirred suspension of PCC (1.5 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> at r.t. was added dropwise a soln. of the alcohol (1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred at r.t. during 3-5 h. The mixture was diluted with an excess of Et<sub>2</sub>O, filtered through a short column of Florisit® (Acros Organics), and evaporated.
- 3. Compounds 6–9. Indane-2-carboxaldehyde (= 2,3-Dihydro-1H-indene-2-carboxaldehyde; 6). According to the G.P.B, indane-2-methanol (14; 3.20 g, purity 97%, 20.9 mmol) was converted to crude 6, to which was added 0.5% (w/w) BHT (= 2,6-di(tert-butyl)-4-methylphenol). Bulb-to-bulb distillation (oven temp. 50–60°/0.2 mbar) afforded 6 (2.10 g, 67%; purity 98%). Colorless oil. IR: 3050, 2910, 2840, 2710, 1720, 1480, 1450, 1450, 140. <sup>1</sup>H-NMR: 9.72 (d, f=2, 1 H); 7.20 (m, 2 H); 7.13 (m, 2 H); 3.24 (m, 3 H); 3.15 (m, 2 H). <sup>13</sup>C-NMR: 202.8 (d); 141.1 (2x); 126.8 (2d); 124.6 (2d); 50.6 (d); 32.9 (2t). MS: 146 (67, M\*), 131 (16), 128 (18), 115 (100), 91 (26), 89 (14), 63 (15), 51 (9), 39 (12), 29 (8).

Indan-2-ylmethyl Acetate (= 2,3-Dihydro-1H-indene-2-methanol Acetate; 15). To a stirred soln, of indane-2-methanol (14; 3.29 g, 22 mmol) in pyridine (25 ml) at r.t. was added Ac<sub>2</sub>O (25 ml), and the mixture was stirred at r.t. during 3.5 h. The mixture was evaporated and the residue co-evaporated  $3 \times 10^{10}$  from toluene. Bulb-to-bulb distillation (oven temp.  $90-100^2/0.8$  mbar) gave 15 (3.98 g, 90%; purity 95%). Colorless oil. 1R: 3015, 2940, 2835, 1730, 1360, 1235, 1040, 745. <sup>1</sup>H-NMR: 7.16 (<math>m, 4 H); 4.10 (d, J=7, 2 H); 3.07 (dd, J=15, 8, 2 H); 2.80 (m, 1 H); 2.73 (dd, J=15, 7, 2 H); 2.06 (s, 3 H). <sup>13</sup>C-NMR: 171.2 (s); 142.3 (2s); 126.4 (2d); 124.6 (2d); 124.6 (2d); 136.6 (36.6); 38.2 (36.6); 38.2 (36.6); 38.2 (36.6); 38.2 (36.6); 38.2 (36.6); 38.2 (36.6); 38.20 (36.6); 38.21 (36.6); 38.21 (36.6); 38.22 (36.6); 38.23 (36.6); 38.23 (36.6); 38.24 (36.6); 38.24 (36.6); 38.24 (36.6); 38.24 (36.6); 38.24 (36.6); 38.24 (36.6); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.24); 38.24 (38.25); 38.24 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.25 (38.25); 38.2

(±)-(5-Acetyl-indan-2-yl)methyl Acetate (= (±)-1-[2-[(Acetyloxy)methyl]-2,3-dihydro-1H-indene-5-yl]-ethanone; 16). To a stirred suspension of AlCl<sub>3</sub> (18.7 g, 140 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 ml) at 20° was added dropwise AcCl (9.9 ml, 140 mmol), and the mixture was stirred at 20° during 1.5 h. The mixture was cooled to 0°, and a soln. of 15 (5.28 g, 27 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added dropwise. The mixture was stirred at 0-4° during 1 h and poured on CH<sub>2</sub>Cl<sub>2</sub>/ice/brine. The org. phase was washed with brine (2×), sat. aq. NaHCO<sub>3</sub> soln., and brine, dried (Na<sub>2</sub>SO<sub>3</sub>), and evaporated to a yellow oil (6.3 g). Bulb-to-bulb distillation (oven temp. 150°/0.4 mbar) gave 16 (5.83 g, 85%; purity 93%). Yellow oil. 1R: 2940, 2830, 1730, 1670, 1600, 1420, 1360, 1235, 1035, 820. <sup>1</sup>H-NMR: 7.80 (d, J = 1, 1 H); 7.77 (dd, J = 8, 1 H); 7.77 (dd, J = 8, 1 H); 4.10 (d, J = 7, 1 H); 3.12 (dd, J = 15, 8, 2 H); 2.86 (m, 1 H); 2.78 (dd, J = 15, 7, 2 H); 2.57 (x, 3 H); 2.06 (x, 3 H). <sup>13</sup>C-NMR: 198.0 (s); 171.1 (s); 148.3 (s); 143.0 (s); 136.1 (s); 127.2 (d); 124.6 (d); 124.5 (d); 67.2 (t); 38.3 (d); 36.0 (t); 35.6 (t); 26.7 (q); 20.9 (q). MS: 232 (1, M \*), 217 (3), 172 (37), 157 (100), 129 (28), 115 (18), 89 (3), 77 (3), 63 (4), 51 (3), 43 (63).

(±)-Indane-2,5-dimethanol (= (±)-2,3-Dihydro-1H-indene-2,5-dimethanol; 17). Bleach (13-14% NaOClin  $H_2O$ ; 21.5 ml, 37.5 mmol) was heated to 55°, and a soln. of 16 (2.91 g, purity 95%, 12.5 mmol) in dioxane (22 ml) was added dropwise during 5 min (slightly exothermic: temp.  $\rightarrow$  70°), and the mixture was heated to 70° during 17 h. The cooled mixture was poured on  $Et_2O$ (sat. aq. NaHSO<sub>3</sub> soln. and  $H_2O$ . The aq. phase was acidified with 10% aq. HCl soln. and extracted with  $Et_2O$ . This org. phase was washed with brine (3×), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to a viscous yellow oil (3.459 g), containing the acid. A soln. of this crude product in THF (50 ml) was added to a stirred suspension of LiAlH<sub>4</sub> (1.75 g, 46 mmol) in THF (30 ml) at r.t. (exothermic: temp.  $\rightarrow$  53°). After 15 h at r.t., the mixture was poured on  $Et_2O$ (10% aq. NaOH soln. The org. phase was washed with sat. aq. NaHCO<sub>3</sub> soln., dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to a solid (2.23 g, 71%; purity 71%). Three crystallizations from AcOE<sub>1</sub> at 0° afforded pure 17. Colorless crystals. M.p. 115.5°. IR (solid): 3352, 3275, 2942, 2905, 2847, 1437, 1359, 1071, 1043, 1021, 821. 'H-NMR (CD<sub>3</sub>OD): 7.16 (br. s, 1 H); 7.12 (d, J = 8, 1 H); 7.07 (d, J = 8, 1 H); 4.87 (s, 2 OH); 4.53 (s, 2 H); 3.51 (d, J = 7, 2 H); 2.98 (m, 2 H); 2.70 (m, 1 H); 2.62 (m, 2 H). '10-NMR

(CD<sub>3</sub>OD): 144.2 (s); 143.1 (s); 140.7 (s); 126.4 (d); 125.3 (d); 124.4 (d); 66.6 (t); 65.4 (t); 43.0 (d); 36.6 (t); 36.4 (t). MS: 178 (52, M<sup>-</sup>), 160 (13), 145 (12), 142 (17), 129 (100), 115 (60), 91 (38), 77 (13), 65 (9), 63 (9), 51 (9), 39 (11), 31 (29).

( $\pm$ )-5-Methylindane-2-methanol (=( $\pm$ )-2,3-Dihydro-5-methyl-IH-indene-2-methanol; 18). According to the *G.P.A.*, with 17 (0.9 g, 5 mmol). Bulb-to-bulb distillation (oven temp.  $\rightarrow$  170°/0.3 mbar) followed by crystallization from pentane at 0° gave 18 (0.64 g, 79%). Colorless crystals. M.p. 41 –41.5°. IR: 3580, 2980, 2910, 1485, 1430, 1025, 995, 810. ¹H-NMR: 7.08 (d, J = 8, 1 H); 7.01 (br. s, 1 H); 6.94 (br. d, 1 H); 3.62 (d, J = 7, 2 H); 3.01 (dd, J = 17, 10, 2 H); 2.68 (m, 3 H); 2.30 (s, 3 H); 1.86 (br. s, OH).  $^{13}$ C-NMR: 142.8 (s); 139.6 (s); 135.8 (s); 127.0 (d); 125.3 (d); 124.3 (d); 66.5 (); 41.6 (d); 35.7 (1); 21.2 (q). MS: 162 (34, M\*), 144 (26), 129 (100), 115 (29), 91 (16), 77 (8), 65 (4), 63 (6), 51 (7), 39 (7), 31 (15).

( $\pm$ )-5-Methylindanc-2-carboxaldehyde (=( $\pm$ )-2,3-Dihydro-5-methyl-1H-indene-2-carboxaldehyde; 7). According to the *G.P.B*, with 18 (0.30 g, 1.9 mmol). Bulb-to-bulb distillation (oven temp. 75%1.15 mbar) afforded 7 (0.24 g, 77%; purity 97%). Colorless liquid. 1R: 3000, 2840, 2700, 1715, 1485, 1430, 805. <sup>1</sup>H-NMR: 9.75 (d, J = 2, 1 H); 7.11 (d, J = 8, 1 H); 7.05 (br. s, 1 H); 6.97 (br. d, J = 8, 1 H); 3.24 (m, 3 H); 3.13 (m, 2 H); 2.31 (s, 3 H). <sup>13</sup>C-NMR: 203.0 (d); 141.3 (s); 138.0 (s); 136.5 (s); 127.6 (d); 125.3 (d); 124.3 (d); 50.9 (d); 32.8 (d); 32.6 (d); 21.2 (d). MS: 160 (100, M \*), 145 (72), 130 (34), 115 (98), 91 (39), 77 (23), 65 (13), 63 (19), 51 (25), 39 (24), 29 (40).

(±)-(5-Ethylindan-2-yl)methyl Acetate (= (±)-5-Ethyl-2,3-dihydro-IH-indene-2-methanol Acetate; 19). According to the G.P.A, with 16. Bulb-to-bulb distillation (oven temp.  $180^\circ$ /0.1 mbar) gave 19 (1.70 g, 88%; purity 94%). Colorless oil. IR: 3000, 2960, 2930, 2840, 1730, 1485, 1435, 1360, 1235, 1035, 820. <sup>1</sup>H-NMR: 7.10 (d, J = 8, 1 H); 7.04 (br. s, 1 H); 6.97 (br. d, J = 8, 1 H); 4.10 (d, J = 7, 2 H); 3.03 (m, 2 H); 2.80 (m, 1 H); 2.70 (m, 2 H); 2.60 (g, J = 8, 2 H); 2.06 (s, 3 H); 1.22 (s, J = 8, 3 H). <sup>13</sup>C-NMR: 171.2 (s); 142.6 (s); 142.5 (s); 139.5 (s); 126.1 (d); 124.4 (d); 124.1 (d); 67.7 (t); 38.4 (d); 35.9 (t); 35.6 (t); 28.7 (t); 20.9 (g); 16.0 (g). MS: 218 (6, M), 158 (45), 143 (56), 129 (100), 115 (31), 91 (8), 77 (5), 65 (3), 63 (3), 51 (3), 43 (32), 39 (4).

( $\pm$ )-5-Ethylindane-2-methanol (=( $\pm$ )-5-Ethyl-2,3-dihydro-1H-indene-2-methanol; 20). To a stirred suspension of LiAlH<sub>4</sub> (0.43 g, 11.3 mmol) in Et<sub>2</sub>O (10 ml) at r.t. was added dropwise a soln. of 19 (1.65 g, purity 94%, 7.5 mmol) in Et<sub>2</sub>O (15 ml), and the mixture was stirred at r.t. during 1.5 h. The mixture was cooled to 0°, 10% aq. NaOH soln. (2.5 ml) was added carefully, and the mixture was stirred during 1 h ( $\rightarrow$  r.t.). Na<sub>2</sub>SO<sub>4</sub> was added and the mixture filtered and evaporated (1.26 g). Bulb-to-bulb distillation (oven temp.  $\rightarrow$  205°/0.1 mbar) gave 20 (1.19 g, 84%; purity > 99%). Colorless oil. IR: 3320 (br.), 3000, 2960, 2920, 2860, 1485, 1430, 1035, 815. <sup>1</sup>H-NMR: 7.10 (d, J=8, 1 H); 7.04 (br. x, 1 H); 6.97 (br. d, J=8, 1 H); 3.63 (d, J=7, 2 H); 3.02 (m, 2 H); 2.69 (m, 3 H); 2.60 (q, J=8, 2 H); 1.94 (br. x, OH); 1.21 (t, J=8, 3 H). <sup>13</sup>C-NMR: 142.9 (s); 142.5 (s); 139.9 (s); 125.9 (d); 124.4 (d); 124.1 (d); 66.6 (t); 6 (5 (t); 41.6 (d); 35.7 (t); 35.4 (t); 28.7 (t); 16.0 (q). MS: 176 (39, M), 158 (15), 143 (67), 129 (100), 115 (34), 91 (12), 77 (7), 65 (4), 63 (5), 51 (5), 39 (5), 31 (10).

( $\pm$ )-5-Ethylindane-2-carboxaldehyde (= ( $\pm$ )-5-Ethyl-2,3-dihydro-1H-indene-2-carboxaldehyde; 8). According to G.P.B, with 20 (1.12 g, 6.4 mmol). Bulb-to-bulb distillation (oven temp.  $\rightarrow$  95°/0.2 mbar) gave 8 (0.85 g, 74%; purity 97%). Colorless oil. IR: 3000, 2960, 2840, 2700, 1715, 1485, 1435, 820. <sup>1</sup>H-NMR: 9.74 (d, J = 2, 1 H); 7.13 (d, J = 8, 1 H); 7.07 (br. s, 1 H); 6.99 (br. d, J = 8, 1 H); 3.24 (m, 3 H); 3.13 (m, 2 H); 2.60 (q, J = 8, 2 H); 1.21 (t, J = 8, 3 H). <sup>13</sup>C-NMR: 203.0 (d); 143.1 (s); 141.3 (s); 138.3 (s); 126.5 (d); 124.4 (d); 124.1 (d); 50.9 (d); 32.6 (t); 28.7 (t); 15.9 (q). MS: 174 (71, M +), 159 (19), 156 (5), 145 (100), 141 (19), 129 (80), 117 (45), 115 (58), 91 (18), 77 (11), 65 (8), 63 (10), 51 (9), 39 (9), 29 (13).

(±)-2-[2-(Ilydroxymethyl)indan-5-yl[propan-2-ol (= (±)-2, $^3$ -Dihydro- $^3$ - $^3$ -dimethyl-IH-indene-2,5-dimethanol; 21). A stirred 22% MeMgCl soln. in THF (16.7 g, 46 mmol; Fluka) at r.t. was diluted with THF (50 ml), and a soln. of 16 (2.92 g, purity 92%, 11.6 mmol) in THF (20 ml) was added dropwise during 5 min (exothermic: temp.  $\rightarrow$  44°). The mixture was heated to 60° during 2 h, then cooled, and poured into Et<sub>2</sub>O/sat. aq. NH<sub>4</sub>Cl soln/ice. The org. phase was washed with sat. aq. NaHCO<sub>3</sub> soln. and brine (2 x), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated (3.14 g). Bulb-to-bulb distillation (oven temp.  $\rightarrow$  200/0.1 mbar) afforded a major fraction (1.76 g, 85%) containing 85% of 21 and 15% of monodehydrated product. IR: 3570, 3400, 2960, 2920, 1430, 1360, 1315, 1160, 1105, 1025, 950, 830. <sup>1</sup>H-NMR: 7.32 (br. s, 1 H); 7.24 (br. d, J = 8, 1 H); 7.13 (d, J = 8, 1 H); 3.61 (d, J = 7, 2 H); 3.02 (m, 2 H); 2.69 (m, 3 H); 2.22 (br. s, OH); 1.55 (s, 6 H). <sup>13</sup>C-NMR: 147.5 (s); 142.8 (s); 141.1 (s); 124.2 (d); 122.5 (d); 120.7 (d); 72.4 (d); 66.3 (d); 41.6 (d); 35.8 (d); 35.3 (d); 31.8 (2d). MS: 206 (16, d), 191 (85), 173 (9), 131 (27), 115 (22), 91 (10), 77 (5), 59 (8), 43 (100), 31 (10).

(±)-5-Isopropylindane-2-methanol (= (±)-2,3-Dihydro-5-isopropyl-1H-indene-2-methanol; 22). According to the G.P.A, with 21 (containing monodehydrated product; 1.90 g, 9.2 mmol). Bulb-to-bulb distillation (oven temp.  $\rightarrow$  140°/0.3 mbar) afforded 22 (1.44 g, 80%; purity 99%). Colorless oil. IR: 3320 (br.), 2960, 2920, 2860, 1485, 1455, 1430, 1030, 815. <sup>1</sup>H-NMR: 7.11 (d, J = 8, 1 H); 7.07 (br. s, 1 H); 7.00 (br. d, J = 8, 1 H); 3.64 (d,

J = 7, 2 H; 3.03 (m, 2 H); 2.87 (sept., J = 7, 1 H); 2.69 (m, 3 H); 1.86 (br. s, OH); 1.23 (d, J = 7, 6 H).  $^{13}$ C-NMR: 147.2 (s); 142.8 (s); 140.1 (s); 124.4 (d); 122.6 (d); 66.5 (d); 41.6 (d); 35.8 (t); 34.0 (d); 24.2 (2q). MS: 190  $(42, M^4)$ , 175 (45), 157 (100), 142 (25), 129 (71), 115 (40), 91 (15), 77 (7), 65 (5), 63 (5), 51 (5), 43 (10), 31 (23).

( $\pm$ )-5-Isopropylindane-2-carboxaldehyde (= ( $\pm$ )-2,3-Dihydro-5-isopropyl-IH-indene-2-carboxaldehyde; 9). According to the *G.P.B.*, with 22 (1.44 g, purity 99%, 7.5 mmol). Bulb-to-bulb distillation (oven temp.  $\rightarrow$  130°0.2 mbar) gave 9 (1.09 g, 74%; purity 96%). Colorless oil. IR: 2950, 2920, 2870, 2700, 1715, 1480, 1430, 1375, 1050, 820. <sup>1</sup>H-NMR: 9.74 (d, J = 2, 1 H); 7.14 (d, J = 8, 1 H); 7.09 (br. s, 1 H); 7.03 (br. d, J = 8, 1 H); 3.25 (m, 3 H); 3.14 (m, 2 H); 1.87 (sept, J = 7, 1 H); 1.23 (d, J = 7, 6 H). <sup>13</sup>C-NMR: 203.0 (d); 147.8 (s); 141.3 (s); 138.5 (s); 125.1 (d); 124.4 (d); 122.5 (d); 50.9 (d); 34.0 (d); 33.9 (t); 32.6 (t); 24.2 (2t). MS: 188 (92, t %), 173 (88), 155 (43), 145 (100), 143 (70), 128 (80), 115 (78), 91 (28), 77 (14), 65 (12), 63 (13), 39 (18), 29 (21).

4. Compounds 10–13. 2-Methylindane-2-carbonitrile (=2,3-Dihydro-2-methyl-1H-indane-2-carbonitrile; 24). To 1.6M BuLi in hexane (58 ml, 93 mmol; Fluka pract.) in THF (40 ml) at −78° was added dropwise within 5 min ¹Pr₂NH (12.5 ml, 88 mmol) and the mixture was stirred at −78° during 30 min. A soln. of indane-2-carbonitrile (=2,3-dihydro-1II-indene-2-carbonitrile; 23; 6.32 g, 44 mmol) in THF (50 ml) was added dropwise within 5 min, and the mixture was stirred at −78° during 1.5 h. The mixture was allowed to warm up to −40°, and MeI (4.2 ml, 66 mmol; Fluka param) was added dropwise. The mixture was stirred during 1 h (−40° → −10°) and then poured on Et₂O/H₂O/ice. The org. phase was washed with 10% aq. HCl soln., H₂O, sat. aq. NaHCO₃ soln., and brine, dried (Na₂SO₄), and evaporated to a yellow liquid (7.25 g). Two bulb-to-bulb distillations (oven temp. 40−65°/0,3 mbar) afforded a product which solidified on standing: 24 (6.14 g, 83%; purity 94%). Crystallization from pentane at 0° gave an anal. sample. Colorless crystals. Mp. 60−60.5°. IR: 2960, 2930, 2840, 2230, 1480, 1450, 1430, 1375. ¹H-NMR: 7.20 (s, 4 H); 3.47 (d, J = 16, 2 H); 3.00 (d, J = 16, 2 H); 1.50 (s, 3 H). ¹³C-NMR: 139.3 (2s); 127.3 (2d); 125.4 (s); 124.7 (2d); 45.5 (2t); 36.9 (s); 25.2 (q). MS: 157 (100, M¹), 142 (75), 130 (73), 115 (79), 105 (10), 103 (10), 89 (18), 77 (16), 63 (22), 51 (19), 39 (18).

2-Methylindune-2-curboxuldehyde (= 2,3-Dihydro-2-methyl-IH-indene-2-curboxuldehyde; 10). To a stirred soln, of 24 (17.7 g, 110 mmol) in toluene (100 ml) at r.t. was added dropwise during 25 min 1.5m DIBAL-H in toluene (120 ml, 180 mmol; Aldrich), while maintaining the temp, at 25° with a water bath. After 1 h at r.t., the mixture was poured slowly into Et<sub>2</sub>O/10% aq. HCl soln-fice. The org, phase was washed with brine, sat. aq. NaHCO<sub>3</sub> soln., and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to a yellow liquid (16.8 g, 95%; purity 99%). Bulb-to-bulb distillation (oven temp,  $55-100^\circ/1.0$  mbar) gave 10. Colorless liquid. IR: 2960, 2920, 2830, 2700, 1720, 1475, 1450, 1425, 745. <sup>1</sup>H-NMR: 7.16 (m, 4 H); 3.34 (d, d = 16, 2 H); 2.74 (d, d = 16, 2 H); 1.28 (d, 3 H). <sup>13</sup>C-NMR: 203.9 (d); 140.9 (2d); 126.8 (2d); 124.7 (2d); 54.2 (d); 40.8 (2d); 20.9 (d). MS: 160 (42, d), 145 (100), 131 (33), 115 (48), 91 (44), 77 (11), 65 (8), 63 (10), 51 (9), 39 (8).

2-Methylindane-2-methanol (= 2,3-Dihydro-2-methyl-1H-indene-2-methanol; 25). To a stirred suspension of LiAlH<sub>4</sub> (3.80 g, 100 mmol) in Et<sub>2</sub>O (50 ml) at r.t. was added during 15 min a soln. of 10 (16.8 g, purity 92%, 100 mmol) in Et<sub>2</sub>O (100 ml). After 1 h at r.t, the mixture was cooled to 4°, and 10% aq. NaOH soln. (19 ml) was added carefully. The mixture was stirred at r.t. during 1.5 h, Na<sub>2</sub>SO<sub>4</sub> was added, and the mixture was filtered and evaporated to a colorless liquid which solidified on standing (13.7 g). Crystallization from pentane at 0° gave 25 (13.4 g, 77%; purity 94%). Colorless crystals. M.p. 47–47.5°. IR: 3350 (br.), 2920, 1450, 1035, 740. <sup>1</sup>H-NMR (360 MHz, CDCl<sub>3</sub>): 7.14 (m, 4 H); 3.48 (s, 2 H); 2.90 (d, J = 16, 2 H); 2.63 (d, J = 16, 2 H); 2.04 (br., OH); 1.16 (s, 3 H). <sup>13</sup>C-NMR (90.5 MHz, CDCl<sub>3</sub>): 142.5 (2s); 126.2 (2d); 124.8 (2d); 70.3 (t); 44.9 (s); 42.7 (2t); 24.0 (t). MS: 162 (25, t), 144 (12), 129 (100), 115 (25), 104 (10), 91 (21), 77 (8), 63 (6), 51 (6), 39 (6), 31 (7)

(2-Methylindan-2-yl)methyl Acetate (= 2,3-Dihydro-2-methyl-IH-indene-2-methanol Acetate; 26). To a stirred soln. of 25 (13.7 g, purity 96%, 79.6 mmol) in pyridine (50 ml) at r.t. was added Ac<sub>2</sub>O (50 ml), and the mixture was stirred at r.t. during 1.5 h. The mixture was evaporated, co-evaporated 3 x from toluene (17.5 g), and bulb-to-bulb distilled (oven temp.  $70 \rightarrow 95^{\circ}/0.3$  mbar): 26 (16.2, 49%; purity >99%). Colorless oil. IR: 2950, 2920, 2830, 1730, 1450, 1365, 1235, 1040, 740. <sup>1</sup>H-NMR: 7.14 (m, 4 H); 2.93 (d, J = 16, 2 H); 2.18 (d, J = 16, 2 H); 2.04 (s, 2 H); 1.17 (s, 3 H). <sup>11</sup>C-NMR: 171.3 (s); 142.1 (s); 126.3 (s); 124.8 (s); 71.3 (s); 43.2 (s); 43.1 (2s); 24.3 (s); 20.9 (s). MS: 204 (1, s), 144 (36), 129 (100), 115 (16), 91 (10), 77 (4), 63 (3), 51 (3), 43 (21), 39 (3).

( $\pm$ )-(5-Acetyl-2-methylindan-2-yl)methyl Acetate (=( $\pm$ )-1-[2-[(Acetyloxy)methyl]-2,3-dihydro-2-methyl-1H-inden-5-yl]ethanone; 27). To a stirred suspension of AlCl<sub>3</sub> (53.3 g, 400 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (200 ml) at 0-4° was added within 13 min AcCl (28.4 ml, 400 mmol), and the mixture was stirred at 4° until the AlCl<sub>3</sub> was dissolved (5 min). A soln. of 26 (16.2 g, 79.6 mol) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was added dropwise during 15 min, while maintaining the temp. at ca. 4°, and the mixture was stirred at ca. 4° during 1 h. The mixture was added to CH<sub>2</sub>Cl<sub>2</sub>/brinefice, the org. phase washed with brine (2×), sat. aq. NaHCO<sub>3</sub> soln., and brine, dried (Na<sub>2</sub>SO<sub>4</sub>),

and evaporated to a green oil (18.2 g). Bulb-to-bulb distillation (oven temp. 145  $\rightarrow$  200°/0.4 mbar) gave 27 (17.5, 89%; purity 96%). Yellow liquid. IR: 2950, 2920, 2830, 1730, 1670, 1600, 1565, 1420, 1355, 1275, 1235, 1040, 825. 

<sup>1</sup>H-NMR: 7.78 (s, 1 H); 7.76 (d, J = 8, 1 H); 7.25 (d, J = 8, 1 H); 2.98 (d, J = 16, 2 H); 2.73 (d, J = 16, 2 H); 2.58 (s, 3 H); 2.06 (s, 3 H); 1.18 (s, 3 H). 

<sup>1</sup>C-NMR: 198.0 (s); 171.2 (s); 148.2 (s); 142.8 (s); 136.1 (s); 127.2 (d); 124.8 (d); 124.7 (d); 70.9 (i); 43.6 (s); 43.1 (i); 42.7 (i); 26.7 (q); 24.2 (q); 20.8 (q). MS: 248 (6,  $M^*$ ), 186 (33), 171 (76), 157 (7), 143 (22), 128 (26), 115 (13), 91 (3), 77 (5), 63 (3), 51 (3), 43 (100), 39 (2).

( $\pm$ )-2-Methylindane-2,5-dimethanol (=( $\pm$ )-2,3-Dihydro-2-methyl-1H-indene-2,5-dimethanol; 28). To stirred bleach (13–14% aq. NaOCl soln.; 34 ml, 59 mmol) at 55° was added a soln. of 27 (4.88 g, purity 95%, 19.8 mmol) in dioxane (40 ml): the reaction was exothermic (temp.  $\rightarrow$  75°) and the mixture became a cloudy emulsion. After 16 h at ca. 64°, the cooled mixture was poured on Et<sub>2</sub>O/sat. aq. NaHSO<sub>3</sub> soln./ice water. The aq. phase was further acidified with 10% aq. HCl soln. in the presence of Et<sub>2</sub>O, and the combined org. phase was washed with brine (3×), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated crude intermediate hydroxy acid (5.72 g), which was used as such for the next step.

To a stirred suspension of LiAlH<sub>4</sub> (2.62 g, 69 mmol) in THF (67 ml) at r.t. was added dropwise within 15 min a soln. of the crude hydroxy acid (5.72 g) in THF (50 ml), and the mixture was heated to reflux (64°) during 16 h. The mixture was cooled to 4°, 10% aq. NaOH soln. (13.1 ml) added cautiously, the mixture stirred during 1 h ( $\rightarrow$  r.t.), Na<sub>2</sub>SO<sub>4</sub> added, and the mixture filtered and evaporated. Flash column chromatography (SiO<sub>2</sub> (200 g), Et<sub>2</sub>Olcyclohexane 9:1) gave 28 (2.83 g, 72%; purity 96%). Colorless syrup. IR: 3300 (br.), 2950, 2850, 1485, 1430, 1365, 1030, 820. <sup>1</sup>H-NMR: 7.14 (s, 1 H); 7.12 (d, J = 8, 1 H); 7.08 (d, J = 8, 1 H); 4.58 (s, 2 H); 3.46 (s, 2 H); 2.87 (d, J = 16, 2 H); 2.60 (d, J = 16, 2 H); 2.36 (br. s, OH); 2.18 (br. s, OH); 1.14 (s, 3 H). <sup>13</sup>C-NMR: 143.0 (s); 142.1 (s); 139.0 (s); 125.4 (d); 124.8 (d); 123.8 (d); 70.2 (l); 65.2 (l); 45.1 (s); 42.6 (l); 42.4 (l); 24.0 (q). MS: 192 (49, M), 174 (14), 159 (19), 143 (52), 129 (100), 115 (38), 105 (15), 91 (49), 77 (16), 65 (8), 63 (7), 51 (8), 39 (11), 31 (25).

(±)-2,5-Dimethylindane-2-methanol (= (±)-2,3-Dihydro-2,5-dimethyl-1H-indene-2-methanol; 29). According to the *C.P.A.*, with 28 (1.68 g, purity 98%, 8.7 mmol). Bulb-to-bulb distillation (oven temp. → 135/0.2 mbar) afforded 29 (1.40 g, 91%; purity 99%). Colorless oil. IR (neat): 3330 (br.), 2910, 1485, 1035, 810. <sup>1</sup>H-NMR (360 MHz, CDCl<sub>3</sub>): 7.04 (d, J = 8, 1 H); 6.98 (br. s, 1 H); 6.93 (br. d, J = 8, 1 H); 3.49 (s, 2 H); 2.87 (d, J = 16 1 H); 2.85 (d, J = 16, 1 H); 2.60 (d, J = 16, 2 H): 2.30 (s, 3 H); 1.80 (s, OH); 1.16 (s, 3 H). <sup>13</sup>C-NMR (90.5 MHz, CDCl<sub>3</sub>): 142.6 (s); 139.4 (s); 135.8 (s); 127.0 (d); 125.5 (d); 124.5 (d); 70.5 (t); 45.0 (t); 42.7 (t); 42.4 (t); 24.0 (t); 21.2 (t). MS: 176 (33, t), 158 (11), 143 (100), 128 (35), 115 (21), 105 (21), 105 (11), 91 (11), 77 (8), 51 (6), 39 (7), 31 (15).

(±)-2,5-Dimethylindane-2-carboxaldehyde (= (±)-2,3-Dihydro-2,5-dimethyl-1H-indene-2-carboxaldehyde; 11). According to the G.P.B, with 29 (0.65 g, purity 99%, 3.7 mmol). Bulb-to-bulb distillation (oven temp. 65°0.2 mbar) afforded 11 (0.62 g, 92%; purity 95%). Colorless oil. IR: 3000, 2950, 2920, 2820, 2690, 1720, 1485, 1450, 1430, 810.  $^{14}$ H-NMR: 9.63 (x, 1 H); 7.07 (d, J = 8, 1 H); 7.02 (br. s, 1 H); 6.97 (br. d, J = 8, 1 H); 3.31 (d, J = 16, 1 H); 3.29 (d, J = 16, 1 H); 2.71 (d, J = 16, 2 H); 2.31 (s, 3 H); 1.28 (s, 3 H).  $^{14}$ C-NMR: 204.0 (d); 141.1 (s); 137.8 (s); 136.4 (s); 127.6 (d); 125.4 (d); 124.4 (d); 54.4 (s); 40.7 (t); 40.5 (t); 21.2 (q); 20.9 (q). MS: 174 (47, M\*), 159 (100), 145 (25), 130 (36), 128 (37), 115 (36), 105 (16), 91 (15), 77 (13), 65 (6), 63 (9), 51 (12), 39 (13), 29 (18).

( $\pm$ )-(5-Ethyl-2-methylindan-2-yl)methyl Acetate (=( $\pm$ )-5-Ethyl-2,3-dihydro-2-methyl-1H-indene-2-methanol Acetate; 30). According to the G.P.A, with 27 (6.1 g, purity 96%, 23.8 mmol). Bulb-to-bulb distillation (oven temp. 130°0.4 mbar) afforded 30 (5.70 g, 99%; purity 96%). Colorless liquid. IR: 3000, 2950, 2920, 2820, 1730, 1480, 1450, 1430, 1380, 1365, 1235, 1035, 820. ¹H-NMR: 7.07 (d, J = 8, 1 H); 2.00 (br. s, 1 H); 6.97 (br. d, J = 8, 1 H); 2.91 (d, J = 16, 1 H); 2.89 (d, J = 16, 1 H); 2.65 (d, J = 16, 1 H); 2.64 (d, J = 16, 1 H); 2.60 (d, J = 7, 2 H); 2.04 (s, 3 H); 1.21 (t, J = 7, 3 H); 1.17 (s, 3 H).  $^{12}$ C-NMR: 171.3 (s): 142.5 (s): 142.2 (s): 139.3 (s): 126.0 (d): 124.6 (d): 124.3 (d): 71.3 (s): 43.3 (s): 43.0 (s): 42.7 (s): 28.7 (s): 24.3 (s): 20.9 (s): 15.9 (s). MS: 232 (7, s). 172 (50), 157 (100), 143 (79), 129 (65), 115 (23), 91 (14), 77 (7), 65 (3), 63 (3), 51 (4), 43 (63), 39 (5).

( $\pm$ )-5-Ethyl-2-methylindane-2-methanol (=( $\pm$ )-5-Ethyl-2,3-dihydro-2-methyl-1H-indene-2-methanol; 31). To a stirred suspension of LiAlH<sub>4</sub> (1.35 g, 35.6 mmol) in Et<sub>2</sub>O (30 ml) at r.t. was added dropwise a soln. of 30 (5.50 g, purity 96%, 23.7 mmol) in Et<sub>2</sub>O (50 ml), and the mixture was stirred during 1 h. The mixture was cooled to 4°, 10% aq. NaOH soln. (6.8 ml) was added cautiously, and the mixture was stirred during 1 h ( $\rightarrow$ r.t.). Na<sub>2</sub>SO<sub>4</sub> was added and the mixture filtered and evaporated to a colorless oil (4.8 g). Bulb-to-bulb distillation (oven temp.  $100-140^{\circ}/0.3$  mbar) gave 31 (4.49 g, 99%; purity 99%). Colorless oil. IR: 3330 (br.), 3000, 2960, 2920, 2860, 2820, 1485, 1450, 1430, 1370, 1035, 820. H-NMR: 7.07 (d, J=8, 1 H); 7.00 (br. s, 1 H); 6.96 (br. d, J=8, 1 H); 3.49 (s, 2 H); 2.87 (d, J=16, 1 H); 2.85 (d, J=16, 1 H); 2.62 (d, J=16, 1 H); 2.61 (d, J=16, 1 H); 2.60

 $(q, J=7, 2 \text{ H}); 1.83 \text{ (br. } s, \text{ OH)}; 1.21 \text{ } (t, J=7, 3 \text{ H}); 1.16 \text{ } (s, 3 \text{ H}). \ ^{13}\text{C-NMR}: 142.7 \text{ } (s); 142.4 \text{ } (s); 139.7 \text{ } (s); 125.9 \text{ } (d); 124.6 \text{ } (d); 124.3 \text{ } (d); 70.6 \text{ } (t); 45.0 \text{ } (s); 42.7 \text{ } (t); 24.4 \text{ } (t); 28.7 \text{ } (t); 24.1 \text{ } (q); 15.9 \text{ } (q). \text{ MS}: 190 \text{ } (55, M^+), 172 \text{ } (18), 157 \text{ } (100), 143 \text{ } (80), 129 \text{ } (80), 115 \text{ } (44), 91 \text{ } (30), 77 \text{ } (13), 65 \text{ } (7), 63 \text{ } (7), 51 \text{ } (8), 39(10), 31 \text{ } (21).$ 

( $\pm$ )-5-Ethyl-2-methylindane-2-carboxaldehyde (=  $\pm$ )-5-Ethyl-2,3-dihydro-2-methyl-IH-indene-2-carboxaldehyde; **12**). According to the *G.P.B.*, with 31 (3.49 g, 18.4 mmol). Bulb-to-bulb distillation (oven temp. 90–125° t 0.4 mbar) afforded 12 (3.31 g, 91%; purity 95%). Colorless oil. IR: 3000, 2960, 2920, 2860, 2820, 2690, 1720, 1485, 1445, 1430, 880, 820. <sup>1</sup>H-NMR: 9.62 (s, 1 H); 7.09 (d, J=8, 1 H); 7.03 (br. s, 1 H); 6.98 (br. d, J=8, 1 H); 3.30 (d, J=16, 1 H); 2.72 (d, J=16, 1 H); 2.71 (d, J=16, 1 H); 2.60 (q, J=7, 2 H); 1.27 (s, 3 H); 1.21 (t, J=7, 3 H). <sup>13</sup>C-NMR: 2040 (d); 143.0 (s); 141.1 (s); 138.1 (s); 126.5 (d); 124.5 (d); 124.1 (d); 54.4 (s); 40.8 (t); 40.5 (t); 28.7 (t); 20.9 (q); 15.8 (q). MS: 188 (56,  $M^*$ ), 173 (100), 159 (49), 145 (47), 129 (62), 115 (46), 91 (30), 77 (16), 63 (11), 51 (12), 39 (13), 29 (18).

(±)-2-(2-(Hydroxymethyl)-2-methylindan-5-yl)-propan-2-ol (=(±)-2,3-Dihydro- $\alpha'$ , $\alpha'$ ,2-trimethyl-1H-indene-2,5-dimethanol; 32). A stirred 22% MeMgCl soln. in THF (32 ml, 95 mmol; Fluka) at r.t. was diluted with THF (100 ml), and a soln. of 27 (5.87 g, purity 95%, 23.8 mmol) in THF (30 ml) was added dropwise during 10 min (exothermic: temp. → 51°). The mixture was heated to 60° during 1.5 h, cooled, and poured on Et<sub>2</sub>O sal. aq. NH<sub>4</sub>Cl soln. ice. The org. phase was washed with sat. aq. NaHCO<sub>3</sub> soln. and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to a cloudy oil which solidified on standing. Crystallization from CH<sub>2</sub>Cl<sub>2</sub> at 0° gave 32 (4.08 g, 76%; purity 98%). Colorless crystals M.p. 122.5−123°. IR (solid): 3264, 2970, 2925, 2860, 1465, 1416, 1360, 1258, 1151, 1030, 956, 911, 841, 820. ¹H-NMR ((D<sub>6</sub>)acetone): 7.32 (br. s, 1 H); 7.25 (br. d, J = 8, 1 H); 7.05 (d, J = 8, 1 H); 3.84 (m, 2 OH); 3.42 (d, J = 6, 2 H); 2.93 (d, J = 16, 1 H); 2.90 (d, J = 16, 1 H); 2.55 (d, J = 16, 1 H); 2.53 (d, J = 16, 1 H); 1.48 (s, 6 H); 1.13 (s, 3 H). ¹¹C-NMR: ((D<sub>6</sub>)acetone): 149.4 (s); 142.3 (s); 141.3 (s); 124.7 (d); 123.3 (d); 121.8 (d); 72.0 (s); 69.9 (t); 46.0 (s); 43.4 (t); 42.9 (t); 32.6 (2q); 24.6 (q). MS: 220 (8, M\*), 205 (45), 202 (4), 145 (17), 128 (13), 115 (11), 91 (8), 59 (12), 43 (100), 31 (9).

(±)-5-Isopropyl-2-methylindane-2-methanol (= (±)-2,3-Dihydro-5-isopropyl-2-methyl-1H-indene-2-methanol; 33). According to the G.P.A, with 32 (4.08 g, purity 98%, 23.8 mmol). Bulb-to-bulb distillation (oven temp.  $125-160^\circ/0.5$  mbar) afforded 33 (3.56, 94%; purity > 99%). Colorless oil. 1R: 3330 (br.), 2960, 2920, 2860, 1485, 1455, 1430, 1375, 1035, 820. H-NMR: 7.07 (d, J=8, 1 H); 7.02 (br. s, 1 H); 6.98 (br. d, J=8, 1 H); 3.48 (s, 2 H); 2.88 (d, J=16, 1 H); 2.85 (d, J=16, 1 H); 2.85 (sept., J=7, 1 H); 2.62 (d, J=16, 1 H); 2.60 (d, J=16, 1 H); 1.26 (d); 12.3 (d, J=7, 6 H); 1.16 (s, 3 H).  $^{13}$ C-NMR: 147.1 (s); 142.6 (s); 139.8 (s); 124.5 (d); 124.4 (d); 122.8 (d); 70.5 (i); 45.0 (s); 42.8 (i); 42.4 (i); 33.9 (il); 24.2 (2q); 24.1 (q). MS: 204 (49,  $M^*$ ), 189 (33), 171 (100), 157 (21), 143 (62), 129 (70), 115 (36), 91 (30), 77 (13), 65 (7), 63 (6), 51 (6), 43 (25), 41 (15), 39 (10), 31 (19).

( $\pm$ )-5-lsopropyl-2-methylindane-2-carboxaldehyde (=( $\pm$ )-2,3-Dihydro-5-isopropyl-2-methyl-1H-indene-2-carboxaldehyde; 13). According to *G.P.B*, with 36 (2.41 g, 11.8 mmol). Bulb-to-bulb distillation (oven temp. 85-145°/0.2 mbar) gave 13 (2.26 g, 93%; purity 98%). Colorless oil. 1R: 2950, 2920, 2850, 2690, 1720, 1485, 1450, 1425, 880, 820. <sup>1</sup>H-NMR: 9.63 (s, 1 H); 7.10 (d, J = 8, 1 H); 7.07 (br. s, 1 H); 7.02 (br. d, J = 8, 1 H); 3.33 (d, J = 16, 1 H); 3.31 (d, J = 16, 1 H); 2.87 (s)-16, 1 H); 2.87 (s)-17, 181; 2.73 (d, J = 16, 1 H); 2.71 (d, J = 16, 1 H); 1.29 (s)-18, 191; 1.22 (d, J = 7, 6 H). <sup>13</sup>C-NMR: 204.0 (d); 147.7 (s); 141.1 (s); 125.1 (d); 124.5 (d); 122.7 (d); 54.3 (s); 40.9 (t); 40.6 (t); 34.0 (d); 24.2 (d2t); 21.0 (d). MS: 202 (d6, d6, d7), 187 (99), 159 (61), 145 (100), 143 (64), 131 (60), 128 (61), 115 (51), 91 (36), 77 (19), 65 (10), 63 (10), 51 (11), 43 (36), 41 (19), 49 (15), 29 (15).

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